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Molecular Dynamics Simulation of Infrared and Raman Spectra of Liquid Methane (Commemoration Issue Dedicated to Professor Tohru Takenaka On the Occasion of His Retirement)

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## Molecular Dynamics Simulation of Infrared and Raman Spectra of Liquid Methane

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Molecular dynamics simulation has been used to investigate the infrared and Raman spectra of liquid methane. The simulation reproduced well the observed spectra in frequency and intensity. These spectra have been compared for harmonic and anharmonic models. Over tones and combination bands are produced for infrared and Raman spectra. Splitting due to Fermi resonance has occurred in the region of  $\nu_1$  coupling with  $2\nu_2$  vibration.

KEY WORDS: Molecular dynamics / Liquid methane / Infrared and Raman spectra

### INTRODUCTION

Infrared and Raman spectra have usually been studied on the basis of normal coordinate analysis and intensity calculation. Recently, molecular dynamics simulation has been applied to produce the spectra, besides studying structure and physical property, of a variety of molecular systems, infrared spectra of CO gas,<sup>1)</sup> Raman spectra of N<sub>2</sub> gas,<sup>2)</sup> infrared spectra of gaseous and liquid SO<sub>2</sub>,<sup>3)</sup> infrared spectra of crystalline benzoic acid,<sup>4,5)</sup> and molten LiNO<sub>3</sub>.<sup>6,7)</sup> These spectra reproduced well the observed ones in frequency, intensity, band shape and splitting due to intermolecular interactions.

In a previous paper,<sup>8)</sup> physical properties of liquid methane were studied by using molecular dynamics simulation. The simulation reproduced well the radial distribution and the self-diffusion coefficient and suggested cooperative rotational motion as a gear wheel. In this work, infrared and Raman spectra of liquid methane simulated by the method are reported.

### METHOD AND MODEL

The method of the simulation and the model of the system are described in a previous paper.<sup>8)</sup> Two kinds of models are adopted; one is a harmonic model, the other is an anharmonic model. In the harmonic model, quadratic force constants, listed in Table I of the previous paper,<sup>8)</sup> are used. In addition, cubic and quartic force constants for the CH stretching coordinate are introduced for the anharmonic model.

Infrared spectra are obtained from the linear response equations<sup>1)</sup>

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$$\alpha_d(\omega) = \frac{4\pi^2\omega^2\beta}{3cn} I_d(\omega), \quad d=x, y, z \quad (1)$$

and

$$I_d(\omega) = \frac{3}{2\pi} \left[ \lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \left| \int_{-\tau}^{\tau} dt \exp(-i\omega t) \mu_d(t) \right|^2 \right], \quad d=x, y, z \quad (2)$$

where  $\alpha_d(\omega)$  is the absorption cross section as a function of angular frequency  $\omega$ ,  $\beta = (k_B T)^{-1}$  in which  $k_B$  is Boltzmann's constant and  $T$  is the temperature,  $c$  is the velocity of light, and  $n$  is the refractive index of the medium.  $I_d(\omega)$  is defined as the absorption band shape, and may be computed in the form of the power spectrum by fast Fourier-transform technique. The equations are written in the form applicable to oriented systems and can be used for isotropic systems by taking an average of the three  $\alpha_d(\omega)$ .

Dipole moment of the system  $\mu_d$  is obtained by summing over bond dipoles  $\mu_k$  of all molecules in the system.

$$\mu_d = \sum_{mol} \sum_{bond} \mu_k \Phi_d \quad (3)$$

where  $\Phi_d$  is direction cosine between  $k$ th dipole and  $d$ th axes. Bond dipole is assumed as follows:

$$\mu_k = \mu_k^0 + \sum_j \frac{\partial \mu_k}{\partial S_j} S_j \quad (4)$$

in which  $S_j$  is  $j$ th internal coordinate,  $\mu_k^0$  is  $k$ th bond moment at equilibrium, and  $\partial \mu_k / \partial S_j$  means charge flux in  $k$ th bond induced by  $j$ th internal coordinate. Values of parameters are listed in Table 1 in the units of electronic charge and Angstrom.

The differential cross section of Raman scattering is calculated by the following equation.

$$\left( \lambda_s^4 \frac{d^2 \sigma}{d\omega d\Omega} \right)_{FF'} = \frac{1}{2\pi} \left[ \lim_{\tau \rightarrow \infty} \frac{1}{2\tau} \left| \int_{-\tau}^{\tau} dt \exp(-i\omega t) P_{FF'}(t) \right|^2 \right] \quad (5)$$

where  $d\omega$  is angular frequency range,  $d\Omega$  is solid angle range.  $F$  and  $F'$  are space fixed coordinates. When  $F=F'$ , parallel spectra are obtained, and if  $F \neq F'$ , perpendicular spectra are evaluated. Polarizability of the system  $P_{FF'}$  is obtained by summing over the bond polarizability  $P_i$  of all molecules in the system.

$$P_{FF'} = \sum_{mol} \sum_{bond} \sum_i P_i \Phi_{Fi} \Phi_{F'i} \quad (6)$$

in which  $P_i$  is principal polarizability fixed to the  $k$ th bond.  $\Phi$  is direction cosine. Cylindrical polarizability is assumed, that is,  $P_1$  is polarizability parallel to a bond,  $P_2=P_3$  is polarizability perpendicular to the bond. Bond polarizability is assumed to be

$$P_i = P_i^0 + \sum_j \frac{\partial P_i}{\partial S_j} S_j \quad (7)$$

where  $P_i^0$  is bond polarizability at equilibrium with respect to  $i$ th principal axes of polarizability, and  $\partial P_i / \partial S_j$  is derivatives of the bond polarizability with respect to the  $j$ th internal coordinates of a molecule. Values of the parameters estimated from the observed polarizability of 2.61 and literature values,<sup>9)</sup> are also listed in Table 1.

Table 1. Electro optical parameters

$\mu_k^0$	0.241	$a_1^0$	0.8412
$\partial \mu_k / \partial r_k$	-0.922	$\alpha_2^0 (= a_3^0)$	0.5582
$\partial \mu_k / \partial r_j$	-0.234	$\partial \alpha_1 / \partial r_k$	2.5196
$\partial \mu_k / \partial \theta_{kj}$	-0.028	$\partial \alpha_2 / \partial r_k$	0.4186
		$\partial \alpha_1 / \partial r_j$	-0.0906
		$\partial \alpha_2 / \partial r_j$	0.0453

## RESULTS AND DISCUSSION

### Infrared spectra

Methane molecule has  $T_d$  symmetry, and four fundamental vibrations as follows:

$$A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3, \nu_4)$$

$F_2$  species is infrared active, and  $A_1$ ,  $E$  and  $F_2$  species are Raman active. Figure 1 demonstrates a simulated infrared spectrum of an anharmonic model of liquid methane. The  $\nu_3$  and  $\nu_4$  bands are seen in the figure as expected from selection rule. The effect of anharmonicity are detected in frequency, half band width, and intensity as listed in Table 2. Anharmonicity acts to lower frequency and widen the band width for the stretching vibration  $\nu_3$  whose potential function include anharmonicity. The frequency may depend on amplitudes which are populated by Boltzmann factor. However, the bending vibration  $\nu_4$  was not affected by anharmonicity both on frequency and half band width, because the bending coordinate is treated as harmonic. Intensity for two models are the same order to the observed.

Figure 2 displays the simulated infrared spectra of an anharmonic model in the region of overtone and combination bands. Considering the  $F_2$  species is infrared active, assignments of bands are given as indicated in the figure. The  $\nu_1 + \nu_3$  combination band of stretching modes appears in the case of anharmonic model, but disappears for harmonic model. The overtone of a bending vibration  $\nu_4$  appears without anharmonic term in force field. The bending mode depicts an arc and results in transition dipole of the frequency of  $2\nu_4$  in the direction of the bond.

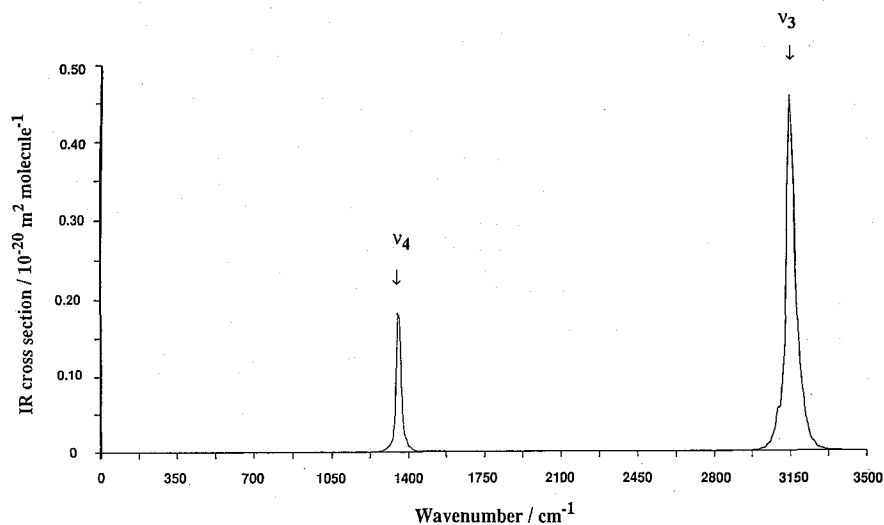


Fig. 1. Simulated infrared spectrum of an anharmonic model of liquid methane in the region of fundamentals.

Table 2. Calculated and experimental frequencies and band widths of  $\nu_3$  and  $\nu_4$  infrared bands

	Wavenumber / $\text{cm}^{-1}$			Half band width / $\text{cm}^{-1}$			Intensity / $\text{km mol}^{-1}$		
	harm.	anharm.	exp. <sup>10)</sup>	harm.	anharm.	exp. <sup>11)</sup>	harm.	anharm.	exp. <sup>10)</sup>
$\nu_3$	3169	3154	3152	24	44	40	11700	14300	6729
$\nu_4$	1357	1357	1361	24	24		4300	2900	3365

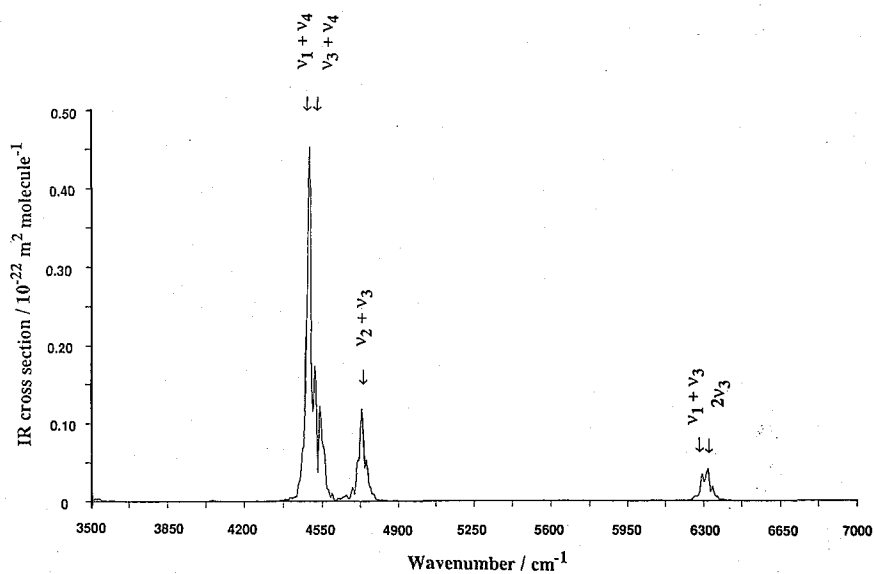


Fig. 2. Simulated infrared spectrum of an anharmonic model of liquid methane in the region of overtones and combinations.

**Raman spectra**

All fundamental vibrations of methane are Raman active, although totally symmetric vibration  $\nu_1$  is strong in intensity. Figures 3 and 4 display the simulated Raman spectra of harmonic model of liquid methane. The  $\nu_1$  band splits into two components. It may be due to Fermi resonance of  $\nu_1$  and  $2\nu_2$  modes. Parallel component of the band is strong as expected for  $A_1$  species.

The  $\nu_2$  band is weak, and an enlarged spectrum is shown in Fig. 4. Although statistical noises are considerably large, depolarization ratio is close to the theoretical value of  $3/4$ .

The  $\nu_3$  (E symmetry species) band is close to the  $\nu_1$  band, and parallel component may be hid by the  $\nu_1$  band. As the  $\nu_4$  ( $F_2$  symmetry species) is very weak and near to the  $\nu_2$  band, the position of the mode is indicated in the figure. The  $2\nu_4$  appears clearly, showing parallel polarization. Symmetry species of the overtone  $2\nu_4$  consists of

$$(F_2)^2 = A_1 + E + F_2$$

The depolarization ratio may close to zero, as  $A_1$  symmetry species is included.

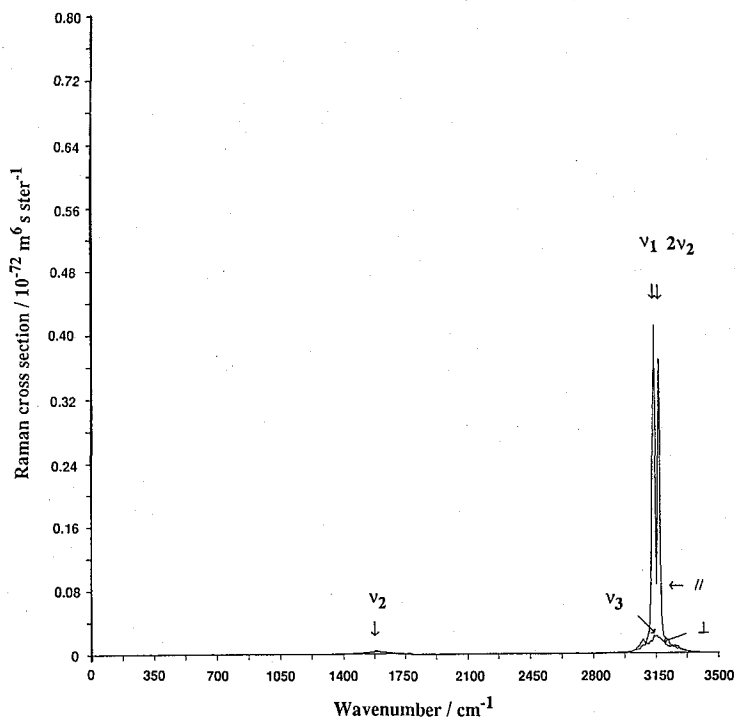


Fig. 3. Simulated Raman spectra of a harmonic model of liquid methane.

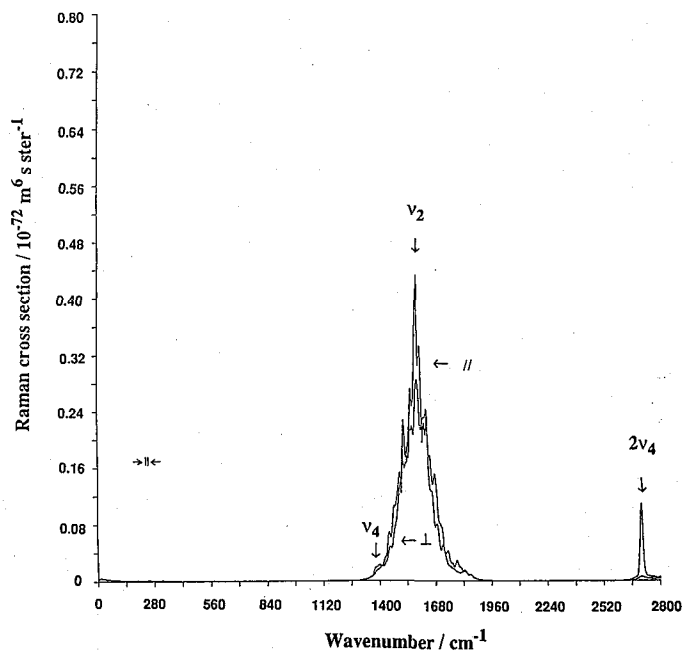


Fig. 4. Enlarged spectra of Fig. 3.

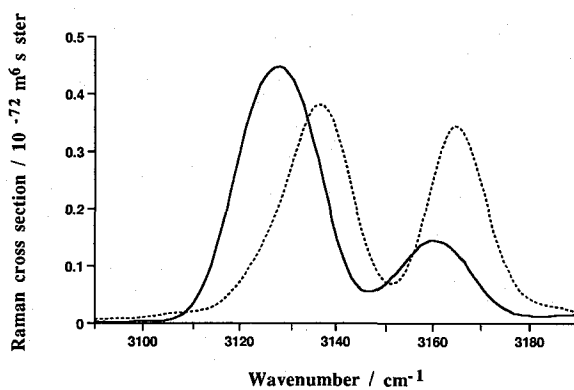


Fig. 5. Simulated Raman spectra of a harmonic (—) and an anharmonic (.....) models of liquid methane in the region of stretching vibration.

Table 3. Effects of anharmonicity on the  $\nu_1$  and  $2\nu_2$  Raman bands

Wavenumber / cm <sup>-1</sup>			Half band width / cm <sup>-1</sup>	
harm.	anharm.	exp. <sup>9)</sup>	harm.	anharm.
3137	3129	3136	16.4	20.4
3166	3162	3166	14.1	18.8

Figure 5 shows the Raman spectra of the harmonic and anharmonic models of liquid methane, respectively, in the  $\nu_1$  and  $2\nu_2$  region. Anharmonicity acts to lower frequency and widen half band width for stretching vibration as shown in Table 3, however, dose not affect for bending mode as described above. The lower frequency band is contributed predominantly by the  $\nu_1$  mode and become stronger than the higher band. This is reasonable because integration of intensity of the two bands is similar for the harmonic and anharmonic models. Observed spectra shows strong  $\nu_1$  band and weak  $2\nu_2$  band. Difference between the observed and simulated spectra may be caused by deference of  $\nu_2$  frequency. A slight increase of the bending force constant may improve the simulated spectra.

### CONCLUSION

Molecular dynamics simulation has been used to investigate the infrared and Raman spectra of a harmonic and an anharmonic models of liquid methane. The simulation reproduced well the observed spectra in frequency and intensity. Overtone and combination bands of stretching modes are produced for infrared and Raman spectra for anharmonic model. On the other hand, these of bending models are produced for both harmonic and anharmonic models. Fermi resonance has occurred for coupling between the  $\nu_1$  and  $2\nu_2$  modes.

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**Erratum**

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Page 171, Figure caption of Fig. 5 should be the following:

Simulated Raman spectra of a harmonic (-----) and an anharmonic (——) models of liquid methane in the region of stretching vibration.